1,008,126

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Photoconductive Compositions for use in Electrostatic Printing

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

THIS INVENTION relates to new photoconductive coating compositions, to bases coated with them and to a process for electrostatic printing using such coated bases as recording elements.

In the art of electrostatic printing a latent electrostatic image is produced on a photoconducting insulating material by any of a number of procedures recognized in the art This may be accomplished by first producing on the surface of the material a substantially uniform electrical charge, for example by exposure to a Corona discharge. The charged material (otherwise known as the recording element) is then exposed to a pattern of light and shadow illumination whereby the illuminated areas are discharged and a charge image remains which corresponds to the pattern presented to the recording element. Visible images are then produced by the application under electrostatic attraction of finely-divided developer particles to the charge image. The application can be by a number of methods known to the art, for example by the use of dry particles of solid material, such as carbon particles or iron filings, applied by either the cascade development method or by the powder cloud development method, or by applying a liquid or solid developer containing finely-divided developer particles to the charge image surface.

Recording elements previously used in electrostatic printing processes have comprised a base member, such as paper, coated with an electrically-insulating photoconductive layer such as photoconductive zinc oxide suspended in an insulating binder. As binders there have been used various resins, for example styrene-butadiene copolymers and resinous polysiloxanes (silicones). However, resinous binders of the silicone or styrene-butadiene copolymer type are relatively viscous, thermoplastic materials, and consequently must be formulated as aqueous dispersions or as solutions in liquid hydrocarbons in order to render them sufficiently fluid for application to the base material. Moreover, the silicone binders are expensive and thus are not suitable for use on a commercial scale.

The success of an electrostatic printing process depends, first, on the ability of the recording element to accept a relatively high over-all voltage charge; secondly, on its ability to give up the charge immediately on exposure to light, and to discharge quantitatively in proportion to the amount of light to which it is exposed; thirdly, to retain the full charge for substantial periods, sufficient to effect their development, in the portions which have been unexposed or only partially discharged by exposure to light; and fourthly, to produce a final visible image of good contrast and difinition. These requirements necessitate the presence of a high concentration of a photoconductive pigment particles on the surface of the recording element, and also the presence of a highly non-conductive electrically insulating binder to prevent premature discharge of the originally imposed charge.

The photoconductive coatings of the prior art, in general, were not suitable for providing, in a single conventional coating application, coatings containing more than about 40 percent of photoconductive pigment particles, due to the high viscosities of the binders used and the use of volatile solvents to achieve consistencies suitable for coating applications. Such coatings were often slow

to discharge upon exposure to light, and hence ineffective in the production of satisfactory images. Previous efforts to overcome this difficulty by the application of multiple coats have not been successful. Moreover, the prior art coating compositions, as described above, were incapable of being applied rapidly to the base due to the time required to eliminate the aqueous diluent or organic solvent.

We have now devised, according to the present invention, photoconductive insulating coating compositions which can be conveniently applied to bases by hot melt coating in the preparation of recording elements. The compositions of the invention comprise at least 60% of a finely-divided photoconducing substance dispersed in a hydrocarbon wax having an average molecular weight of 1,000 to 3,000, said composition being solid at temperatures up to 95°C. but being sufficiently liquid at elevated temperatures to be applied to a substrate by the curtain coating method.

The hydrocarbon wax may be composed of (i) polyethylene wax components entirely within the 1,000-3,000 molecular weight range or it may be composed of a blend of (ii) a hydrocarbon wax component of molecular weight below this range with (iii) polyethylene of molecular weight above this range or a blend of (i) polyethylene wax of the desired molecular range with either of components (ii) or (iii) in suitable proportions to provide the specified average molecular weight. A particularly desirable composition of the above type comprises at least 60% of photoconductive finely-divided zinc oxide dispersed in normally solid wax comprising at least 90% of a polyethylene wax of molecular weight between about 1,000 and about 3,000, said composition having a melt viscosity at a temperature of 149°C., sufficiently low for application as a hot melt coating by a conventional curtain or roller coater. By "normally solid hydrocarbon wax" as used in this specification is meant a hydrocarbon wax—that is, a waxy material consisting of carbon and hydrogen—which is a solid at ordinary room temperatures.

Although the compositions of the invention may have melt viscosities of 6000 centipoises or more when tested by the Brookfield viscosimeter at spindle speeds of 60 r.p.m., they can nevertheless be used effectively in conventional manner as hot melt coatings in curtain or roller coaters, which usually are considered capable of handling coatings of viscosities only up to 2,000 or 3,000 centipoises. The compositions of the invention can be applied to a paper or other base as a hot melt coating, especially in an amount of 20 pounds of composition per ream of paper, followed by cooling the resulting coated paper to solidify the coating.

In preparing the coating compositions according to a preferred embodiment of this invention, the polyethylene wax is melted in a suitable container equipped with agitation means, for example a colloid mill or other suitable blender. Photosensitive zinc oxide in finely-divided form is added to the stirred melt, preferably gradually, and agitation is continued until the components are thoroughly blended. After blending, it may be desirable to allow the mixture to stand for a short period to permit release of any bubbles which may have become entrapped in the mixture. Other additives may be blended at this point if desired, but should not exceed about 10% of the total carrier portion of the composition and should not be of a character to adversely affect the electrical properties of the resulting composition or to unduly increase its melt viscosity.

Compositions consisting solely of photosensitive zinc oxide and polyethylene wax are satisfactory for many electrostatic printing applications. For other applications it may be desirable to include additional components such as dyes, toners, and tackifiers (for instance polyisobutlylene or a terpene resin). Flow modifiers and other additives may be included in small proportions as necessary.

The polyethylene wax used is a normally solid polymer of ethylene having an average molecular weight between 1,000 and 3,000, melting point between about 95°C. and about 115°C., and having a viscosity at 140°C. of not more than about 1,000 centipoises, preferably between 50 centipoises and 250 centipoises. Polyethylene waxes having average molecular weights between 1,000 and 3,000 and prepared according to United States Patents No. 2,504,400 and No. 2,683,141 are especially suitable.

Any finely divided, pulverulent photosensitive zinc oxides can be used, but those having an average particle size of 0.39 to 0.41 micron are especially suitable.

The proportions of the components in the composition are important. To ensure the acceptance and maintenance of the required voltages, and to provide satisfactorily reproduced images, the photosensitive zinc oxide should be present in at least 60% by weight of the total composition, preferably in amounts between 65% and 85%. Compositions containing less than 60% zinc oxide fail to provide reproduced final images of satisfactory contrast and definition, while compositions containing more than 85% zinc oxide become increasingly thixotropic and too thick for application to substrates by conventional coating processes.

The polyethylene wax employed, surprisingly provides an excellent suspending medium for even the high loadings of zinc oxide required for electrostatic purposes. While such compositions tend to be somewhat thixotropic, under the agitation imposed by the application techniques of the coaters they

yield homogeneous, free-flowing, low viscosity compositions at temperatures above the melting point of the wax, and suitable for the hot melt coating of paper or other bases by the use of conventional hot melt coating equipment.

The compositions of this invention have apparent viscosities, as measured in a Brookfield rotation viscometer, which reflect to some extent their thixotropic character. For example, compositions having apparent viscosities up to about 10,000 centipoises measured in a Brookfield viscometer at 149°C. using a 30 RPM spindle are satisfactory for application by means of the standard hot melt coating process where they are broken down to an actual viscosity of about 1,000 to 2,000 centipoises at the point of application.

The compositions of this invention can be applied to the base (substrate), which may be paper, cloth, or the like, by any of the conventional hot melt coating devices, for example by means of a Mayer Coater or a Steinemann Coater. In the Mayer Coater, the paper or other substrate is led over a roll dipping in a trough of the hot, molten coating composition. The roll picks up coating from the pool and applies it to the travelling web, the excess being removed by a doctor roll. The coated web is then passed over a chilled roll which sets the coating on the substrate.

In coaters of the type of the Steinemann Coater, the molten coating is passed through a slot positioned obove the travelling web of substrate, forming a curtain of molten coating composition which flows onto the substrate. Excess may be removed by a doctor blade if desired. Other conventional hot melt coating processes and equipment may be employed if desired.

In order to provide a paper which is capable of accepting and holding an adequate charge at least about 20 pounds of coating per ream of paper (500 sheets 24 x 36 inches) is preferred, preferably from 20 to 40 pounds per ream. For the production of a final permanent visible image of good contrast and satisfactory definition, the coating composition applied should contain at least about 60% zinc oxide by weight, preferably between about 60% and about 85%.

Electrostatic printing of the coated bases of the invention can be carried out in any of the standard electrostatic printing machines by producing a negative electrical charge on the sheet in the dark, preferably using a charge of at least about 200 volts, exposing the charged sheet to a light pattern by any of the conventional photographic procedures. In this step, the charge is lost or reduced in the exposed areas in proportion to the intensity of light reaching the charged surface, thus forming a latent electrostatic image on the sheet. The latent image is developed by applying a pigment powder, which may be pigment alone, such as carbon black or iron filings or a pigmented liquid resin or a pigmented resin powder. In any case, the powder carries an electrostatic charge and is attracted to the oppositely charged image and held thereon. The powder image is then fixed by suitable means, for example as by pressure or by melting the resin powder so that it fuses to the paper and produces a durable, light fast image.

There follow Examples which illustrate the invention, in comparison with Examples of compositions not according to the invention, the "parts" referred to being by weight except where otherwise stated.

EXAMPLES 1-5

Five coating compositions were prepared by melting portions of polyethylene wax of molecular weight about 1,500 melting point (ASTM E-28-51-T) 99-103°C., hardness 6-9 (ASTM D-1321-55-T), specific gravity 0.91 and viscosity at 140°C of 100 centipoises, and mixing therewith in a colloid mill at a temperature between 149°C. and about 177°C. portions of photoconductive zinc oxide (New Jersey Zinc Co. "PHOTOX" 801) of average particle size about 40 microns, in the proportions shown in Table I below. Each of the coating compositions was heated to 149°C. and applied to 22 pound sulphite "waxing" paper, (that is unwaxed paper suitable for waxing) by hot melt application from either a standard Mayer Coater or a standard Steinemann Coater at different weights of coating, and cooled to set the coating.

The resulting coated papers were tested for efficiency of reproduction in an electrostatic printing machine as follows. The coated papers were given an electrical charge by passing a bar at about 500 volts across them. Light was then passed through a printed sheet to be copied, onto the charged paper, thereby dissipating the charge in proportion to the light reaching the paper, and forming a latent electrostatic image thereon. Iron filings dispersed in a low melting resin were then spread on the paper and adhered to the charged portions of the paper, rendering the latent image visible. Excess filings were

brushed off and the filings remaining on the paper were fused to the image by heating at about 71°C. for 30-60 seconds.

Compositions used in the tests, as well as manner of application and results, are shown in Table I below:

TABLE I

Example No.	Parts by Weight				
	1	2	3	4	5
Polyethylene wax	50	50	50	40	35
Zinc oxide	50	50	50	60	65
Coating weight lb./ream	11	20	25	25	35
Coating machine	Mayer	Mayer	Steinemann	Steinemann	Steinemann
Reproduction	Poor	Unsatisfactory	Unsatisfactory	Satisfactory	Excellent

It will be noted that the coatings which contained only 50% of zinc oxide produced recording papers which yielded unsatisfactory images on reproduction, even when applied at a total coat weight of 25 pounds per ream. The coatings of only 11 pounds per ream (5.5 pounds of photoconductive zinc oxide per ream) gave especially poor reproduction. Those deposited at 20 and 25 pounds of total coating per ream gave a slightly improved, but still unsatisfactory coatings. On the other hand, a coating containing 60% zinc oxide applied at 25 pounds per ream gave satisfactory reproduction, and a coating containing 65% zinc oxide, applied at 35 pounds per ream, gave excellent reproduction.

The several coated papers were also checked for voltage decay and rate of discharge on an oscilloscope. In this test the coated papers were given a 500 volt charge and then were placed in the oscilloscope for 2 minutes and voltage decay noted. All the coated papers maintained their charge of 500 volts substantially unchanged during the test. The sheets were then given a reverse charge, and all discharged substantially instantaneously, i.e. in substantially less than 1 second.

EXAMPLE 6

Four samples of paper coated with a composition consisting solely of polyethylene wax of 2,000 molecular weight and various proportions of photochemical zinc oxide, ranging from 60% to 80% of the total composition, were subjected to a 500 volt charge and placed in an oscilloscope for 2 minutes (about the maximum time required for reproduction of an image in electrostatic printing machines), and the voltage decay was determined. The charge on the papers was then reversed and the time required to discharge to zero was noted. To test the quality of image reproduction, other samples of the same papers were charged with 500 volts, exposed to identical light patterns to produce an electrostatic image and the image was then developed by brushing with a resin powder pigmented with iron filings. The paper was inverted to remove non-adhering particles, then heated for 30 to 60 seconds at 71°C., whereby the adhering filings were fused to the image portions of the paper. Each coated sample was tested by writing thereon with a ball point pent to test its markability. For comparison, a sample of paper was similarly coated with a composition consisting of the

same wax and 50% zinc oxide, the comparison samples being tested in the same way.

Results of these tests are recorded in Table II below.

TABLE II

% ZnO in Coating	Markability	Voltage after 2 mins.	Discharge Time	Character of Reproduction of Image
a) 50	No	480	Immediate*	Unsatisfactory
b) 60	No	480	,,	Satisfactory
c) 65	Yes	480	,,	Good
d) 70	Yes	480	,,	Very Good
e) 80	Yes	480	,,	Excellent

* Less than 1 second.

It will be noted from Table II that all the polyethylene wax-zinc oxide coatings containing 65% of pigment or more can be written on with ordinary ball point pen. All the coatings maintain their initial voltage substantially unchanged for a least 2 minutes and all discharge immediately upon reversal of charge.

All the coatings comprising 60% or more of photosensitive zinc oxide pigment in the coating give acceptable reproduction of the electrostatic image, those of higher proportion of pigment yielding superior images.

EXAMPLE 7

A coating composition was prepared by melting in a colloid mill 35 parts of a polyethylene wax having an average molecular weight of 2,000, melting point about 104-108°C. and viscosity at 140°C. of 180 centipoises. The temperature of the melted wax was raised to 149-177°C. and maintained in this temperature range during gradual addition with agitation, of 65 parts of photosensitive zinc oxide of particle size 0.40 micron. After completion of addition of zinc oxide, agitation and temperature were maintained for about an hour to thoroughly blend the components. After blending, the coating composition was allowed to stand quiescent at 149°C. until gas bubbles, which had become entrapped during mixing, were substantially dissipated.

The resulting composition was tested for apparent viscosity in a Brookfield viscometer at various temperatures and spindle speeds with results shown in Table III below.

TABLE III

Spindle Speed RPM	Temp. °C.)	Apparent Viscosity Centipoises)
12	149	12,200
	160	11,800
	177	11,200
30	149	8,200
	160	7,700
	177	7,000
60	149	6,100
	160	5,800
	177	5,200

The compositions of the invention, thus have excellent electrical properties and they maintain the zinc oxide in excellent suspension. They have fair adhesion to the paper substrate which can be improved by the addition of small quantities of compatible tacky modifiers, such as polybutene and tacky resins of the terpene type; usually 5-10% or less of such tackifiers are sufficient. If desired, small proportions of toners or other additives may be used, but these should be of such character as not to detract from the desirable electrical properties of the coating or unduly increase its melt viscosity. In general, not more than about 10% of the vehicle of the coating composition should be made up of such additives, and at least about 90% of the total binder will consist of polyethylene wax.

WHAT WE CLAIM IS:

1. A photoconductive insulating coating composition suitable for use in electrostatic printing, comprising at least 60% by weight of a finely-divided photoconducting substance dispersed in a hydrocarbon wax having an average molecular weight of 1,000 to 3,000, said composition being solid at temperatures up to 95°C. but being sufficiently liquid at elevated temperatures to be applied to a substrate by the curtain coating method.

2. A composition according to claim 1, wherein said wax comprises at least 90% polyethylene wax having a viscosity at 140°C. of 50 to 1,000 centipoises.

3. A composition according to claim 2, wherein the polyethylene wax has a viscosity at 140°C. of 50 to 250 centipoises.

4. A composition according to claim 1, 2 or 3, wherein the photoconductor is zinc oxide.

5. A composition according to claim 4, wherein the zinc oxide is present in an amount of 65-85% by weight of the composition.

6. A composition according to claim 4 or 5, wherein the zinc oxide has an average particle size from 0.39 to 0.41 micron.

7. A photoconductive insulating coating composition substantially as described in any of Examples 4, 5, 6b, c, d or e, and 7.

8. A recording element comprising a base sheet coated with at least about 20 pounds per ream of a composition as claimed in any of the preceding claims.

9. A recording element according to claim 8, wherein the said sheet is of paper.

10. A process for electrostatic printing, which comprises producing a latent electrostatic image on the surface of a recording element as claimed in claim 8 or 9, and thereafter developing said latent image.

11. A process according to claim 10, substantially as described herein.

12. An electrostatic print when obtained by the process of claim 10 or 11.

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RECORDING ELEMENT HAVING POLYETHYLENE WAX BINDER AND ELECTROSTATIC PRINTING THEREWITH

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No Drawing. Filed Dec. 12, 1962, Ser. No. 243,982
8 Claims. (Cl. 96—1.8)

This invention relates to a new coating composition, to a coated base adapted for use as a recording element in electrostatic printing processes, to a process for preparing said base and to a process for electrostatic printing using such recording element.

In the art of electrostatic printing a latent electrostatic image is produced on a photoconducting insulating material by any of a number of procedures recognized in the art. This may be accomplished by first producing on the surface, a substantially uniform electrical charge, as for example, by exposure to a Corona discharge. The charged sensitive recording element is then exposed to a pattern of light and shadow illumination whereby the illuminated areas are discharged and a charge image remains which corresponds to the pattern presented to the sensitive recording element. Visible images are then produced on the charge image surface by the electrostatic attraction of finely divided developer particles to the charge surface. Such developer particles may be presented to the charge image surface of the recording element by a number of methods known to the art, for example, by the use of dry solid material, such as carbon particles, iron filings, etc., known as either cascade development or powder cloud development, or by applying a liquid or solid developer containing finely divided developer particles to the charge image surface.

Recording elements previously used in electrostatic printing processes have comprised a backing member such as paper, coated with an electrically insulating photoconductive layer such as photoconductive zinc oxide suspended in an insulating binder. As binders there have been used liquid dispersions of various resin binders, for example styrene-butadiene copolymers and resinous polysiloxane (silicone) binders.

The resinous binders, including the silicone binders and the styrene-butadiene copolymers are relatively viscous, thermoplastic materials, and consequently must be formulated as aqueous latices or with solvents or thinners such as liquid hydrocarbons in order to render them sufficiently fluid for application to the backing material. The silicone materials in addition are expensive and thus are not adapted for the production of an economic electrostatic printing system.

The success of the electrostatic printing process depends to a large extent, first, on the ability of the recording element to accept a relatively high overall voltage charge, second, on its ability to give up the charge immediately on exposure to light, and to discharge quantitatively in proportion to the amount of light to which it is exposed, third, to retain the full charge for substantial periods, sufficient to effect their development, in the portions which have been unexposed or only partially discharged by exposure to light, and fourth, to produce a final visible image of good contrast and definition.

The above requirements necessitate the presence of a high concentration of photoconductive pigment particles on the surface of the recording element, and also the presence of a highly non-conductive electrically insulating binder to prevent premature discharge of the originally imposed charge.

The prior art recording element coatings, in general, were able to furnish in a single conventional coating application, coatings containing at most not more than about 40 percent of photoconductive pigment particles, due to the high viscosities of the binders used and the requirements for employing volatile solvents to achieve consistencies suitable for coating applications. Such coatings were often slow to discharge upon exposure to light, and hence ineffective in the production of satisfactory images. Efforts to overcome this difficulty by the application of multiple coats were unsuccessful.

Moreover, the prior art coating compositions, as described above, were incapable of rapid application to the paper backing due to the time requirements for eliminating the aqueous or organic solvents, coating application rates ranging, in general, in the vicinity of not more than about 100 feet per minute when applied by a conventional roll coater.

It is an object of the present invention to provide a novel photoconductive insulating coating composition adapted for use in electrostatic printing as a hot melt coating.

It is another object of the invention to provide a novel recording element for electrostatic printing.

It is a further object of the invention to provide a process for preparing recording elements for electrostatic printing wherein a high concentration of photoconductive particles in an insulating binder is applied as a hot melt by conventional coating processes, without the necessity for solvent dissipation or recovery.

A still further object is to provide an improved process for electrostatic printing wherein a high degree of contrast and definition in reproduction is obtained.

These and other objects are accomplished according to my invention wherein a composition comprises at least about 60% of a finely divided photoconductor dispersed in a normally solid polyethylene wax vehicle of average molecular weight between about 1,000 and about 3,000, said composition being solid at temperatures up to about 100° C. and having melt viscosity and thixotropic properties providing sufficient fluidity for coating by the curtain coating method. The polyethylene wax may be composed of polyethylene wax components entirely within the 1,000–3,000 molecular weight range or it may be composed of a blend of polyethylene wax component of molecular weight below this range with polyethylene of molecular weight above this range or a blend of the polyethylene wax with either of the other components in suitable proportions to provide the specified average molecular weight.

A particularly desirable composition of the above type comprises at least about 60% of photoconductive finely divided zinc oxide dispersed in normally solid vehicle comprising at least about 90% of a polyethylene wax of molecular weight between about 1,000 and about 3,000, said composition having a melt viscosity at a temperature of 300° F., sufficiently low for application by hot melt coating in a conventional curtain and/or roller coater.

Although the above compositions may exhibit a melt viscosity of 6000 centipoises or more when tested by the Brookfield viscometer at spindle speeds of 60 r.p.m., they can be used effectively in conventional manner as hot melt coatings in curtain and/or roller coaters, which usually are considered capable of handling coatings of viscosities only up to 2,000 or 3,000 centipoises.

The compositions may be applied to a paper or other backing as a hot melt coating to deposit at least about 20 pounds of coating per ream of paper, and the resulting coated paper is cooled to solidify the coating.

In preparing the coating compositions according to my invention, the polyethylene wax is melted in a suitable container equipped with agitation means. Photosensitive zinc oxide in finely divided form is added to the melt, preferably gradually, while agitating the mixture. Agitation is continued until the components are thoroughly

blended. A colloid mill or other suitable blender may be used for this purpose. After blending, it may be desirable to allow the mixture to stand for a short period to permit release of any bubbles which may have become entrapped in the mixture. Other additives may be blended at this point if desired, but should not exceed about 10% of the total vehicle portion of the composition and should not be of a character to adversely affect the electrical properties of the resulting composition or to unduly increase its melt viscosity.

Compositions consisting solely of photosensitive zinc oxide and polyethylene wax are satisfactory for many electrostatic printing applications. For other applications it may be desirable to include additional components such as dyes, toners, etc., tackifiers, such as polyisobutylene or adhesive resins, such as, for example, the terpene resins. Flow modifiers and other additives may be included in small proportions as necessary.

The polyethylene wax used as the binder in my electrostatic printing composition is a normally solid polymer of ethylene having an average molecular weight between about 1,000 and about 3,000, melting point between about 95° C. and about 115° C., and viscosity at 140° C. of not more than about 1,000 centipoises, preferably between about 50 centipoises and about 250 centipoises. The polyethylene waxes having average molecular weights between about 1,000 and about 3,000 prepared according to U.S. Patents of Michael Erchak, Jr., No. 2,504,400, issued Apr. 18, 1950, and No. 2,683,141, issued July 6, 1954, are especially suitable.

These patents describe waxes prepared by polymerizing ethylene in contact with isopropanol. Studies of the reactions of these products indicate that the structural formulae of the compounds making up the waxes formed in isopropanol may be written

$$CH_3(C_2H_4)_nC(OH)(CH_3)_2$$

wherein n is an integer. These waxes are a mixture of individual homologs having varying individual values for n, substantially all of said individual values for n being in the wax range.

Any finely divided, pulverulent photosensitive zinc oxides can be used, and those having a particle size in the range between about 0.39 micron and about 0.41 micron are especially suitable.

The proportions of components in my electrostatic printing composition are important, and for assuring the acceptance and maintenance of the required voltages, and for providing satisfactorily reproduced images I find that the photosensitive zinc oxide must be present in at least about 60% by weight of the total composition, preferably in amounts between about 65% and about 85%. Compositions containing less than about 60% zinc oxide fail to provide reproduced final images of satisfactory contrast and definition, while compositions containing more than about 85% zinc oxide become increasingly thixotropic and too thick for application to substrates by conventional coating processes.

The polyethylene wax employed, surprisingly provides an excellent suspending medium for even the high loadings of zinc oxide required for electrostatic purposes. While such compositions tend to be somewhat thixotropic, they readily break down under the agitation imposed by the application techniques of the coaters and yield homogeneous, free-flowing, low viscosity compositions at temperatures above the melting point of the wax, adapted for hot melt coating of paper or other substrate through the use of conventional hot melt coating equipment.

The coatings of my invention have apparent viscosities, as measured in a Brookfield rotation viscometer, which reflect to some extent the thixotropic character of the compositions. I have found that coatings having apparent viscosities up to about 10,000 centipoises measured in a Brookfield viscometer at 300° F. using a 30 r.p.m. spindle are satisfactory for application by means of the standard hot melt coating process, and are broken down to an actual viscosity in the vicinity of 1,000 to 2,000 centipoises at the point of application.

The coatings of my invention are applied to the substrate, which may be paper, cloth, or the like, by any of the conventional hot melt coating devices, for example, by means of a Mayer Coater, or a Steinemann Coater. In the Mayer Coater, the paper or other substrate, is led over a roll dipping in a trough of the hot, molten coating composition. The roll picks up coating from the pool and applies it to the traveling web, the excess being removed by a doctor roll. The coated web is then passed over a chilled roll which sets the coating on the substrate.

In coaters of the type of the Steinemann Coater, the molten coating is passed through a slot positioned above the traveling web of substrate, forming a curtain of molten coating composition which flows onto the substrate. Excess may be doctored off if desired.

Other conventional hot melt coating processes and equipment may be employed if desired.

In order to provide a paper which is capable of accepting and holding an adequate charge at least about 20 pounds of coating per ream of paper (500 sheets 24" x 36") is required. I preferably apply between about 20 pounds and about 40 pounds of coating per ream. The binder in this weight of coating protects the zinc oxide against undue absorption of moisture which would tend to cause loss of the charge. For the production of a final permanent visible image of good contrast and satisfactory definition, the coating composition applied should contain at least about 60% zinc oxide by weight, preferably between about 60% and about 85%.

Electrostatic printing of the coated paper of my invention can be carried out in any of the standard electrostatic printing machines by producing a negative electrical charge on the sheet in the dark, preferably a charge of at least about 200 volts, exposing the charged sheet to a light pattern by any of the conventional photographic procedures. In this step, the charge is lost or reduced in the exposed areas in proportion to the intensity of light reaching the charged surface, thus forming a latent electrostatic image on the sheet. The latent image is developed by applying a pigment powder, which may be pigment alone, such as carbon black, iron filings, etc., or a pigmented liquid resin or a pigmented resin powder. In any case, the powder carries an electrostatic charge and is attracted to the oppositely charged image and held thereon. The powder image is then fixed by suitable means, for example as by pressure or by melting the resin powder so that it fuses to the paper and produces a durable, lightfast image.

The following specific examples further illustrate my invention. Parts are by weight except as otherwise noted.

Examples 1–5

Five coating compositions were prepared by melting portions of polyethylene wax of molecular weight about 1,500, melting point (ASTM E–28–51–T) 210–217° F., hardness 6–9 (ASTM D–1321–55–T), specific gravity 0.91 and viscosity at 140° C. of 100 centipoises, and mixing therewith in a colloid mill at a temperature between 300° F. and about 350° F. portions of photoconductive zinc oxide (New Jersey Zinc Co. "Photox" 801) of average particle size, about 40 microns, in the proportions shown in the table below. Each of the coating compositions was heated to 300° F. and applied to 22 pound sulfite waxing paper by hot melt application from either a standard Mayer coater or a standard Steinemann coater at different weights of coating, and cooled to set the coating. The resulting coated papers were tested for efficiency of reproduction in an electrostatic printing machine in the following manner. The coated papers were given an electrical charge by passing a bar at about 500 volts across the sheets. Light was then passed through a printed

sheet to be copied, onto the charged paper, dissipating the charge in proportion to the light reaching the paper, and forming a latent electrostatic image thereon. Iron filings dispersed in a low melting resin were then spread on the paper and adhered to the charged portions of the paper, rendering the latent image visible. Excess filings were brushed off and the filings were fused to the image on the sheet by heating at about 160° F. for 30–60 seconds.

Compositions used in the tests, as well as manner of application and results are shown in Table I below:

TABLE I

Example No.	Parts by Weight 1	2	3	4	5
Polyethylene Wax	50	50	50	40	35
Zinc Oxide	50	50	50	60	65
Coating Wt., lbs./ream	11	20	25	25	35
Coater type	(1)	(1)	(2)	(2)	(2)
Reproduction	(3)	(4)	(4)	(5)	(6)

(1) Mayer. (2) Steinemann. (3) Poor. (4) Unsatisfactory. (5) Satisfactory. (6) Excellent.

It will be noted that the coatings which contained only 50% of zinc oxide, produced recording papers which yielded unsatisfactory images on reproduction, even when applied at a total coat weight of 25 pounds per ream. The coatings of only 11 pounds per ream (5.5 pounds of photoconductive zinc oxide per ream) gave especially poor reproduction. Those deposited at 20 and 25 pounds of total coating per ream gave slightly improved, but still unsatisfactory coatings. On the other hand, a coating containing 60% zinc oxide applied at 25 pounds per ream gave satisfactory reproduction, and a coating containing 65% zinc oxide, applied at 35 pounds per ream gave excellent reproduction.

The several coated papers were also checked for voltage decay and rate of discharge on an oscilloscope. In this test the coatings were first given a 500 volt charge. The papers were placed in the instrument and held for 2 minutes and voltage decay noted. All the coated papers maintained their charge of 500 volts substantially unchanged during the entire length of the test. The sheets were then given a reverse charge, and all discharged substantially instantaneously, i.e., in substantially less than 1 second.

Example 6

Five samples of paper coated with a composition consisting solely of polyethylene wax of 2,000 molecular weight and various proportions of photochemical zinc oxide ranging from 50% to 80% of the total composition are charged with a 500 volt charge and placed in an oscilloscope wherein voltage is measured as a function of time. The coatings are held in the oscilloscope for 2 minutes (about the maximum time required for reproduction of an image in electrostatic printing machines) and voltage decay determined. The charge on the papers is then reversed and the time required to discharge to zero is noted. To test the quality of image reproduction, other samples of the same papers are charged with 500 volts, exposed to identical light patterns to produce an electrostatic image and the image is then developed by brushing with a resin powder pigmented with iron filings. The paper is inverted to remove non-adhering particles. The paper is then heated for 30 to 60 seconds at 160° F. whereupon the filings are fused to the image portions of the paper. Each coated sample was tested by writing thereon with a ball point pen to test its markability.

Results of these tests are recorded in Table II below.

TABLE II

Percent ZnO in Coating	Markability	Voltage after 2 min.	Discharge Time	Character of Reproduction of Image
50	No	480	Immediate*	Unsatisfactory.
60	No	480	do	Satisfactory.
65	Yes	480	do	Good.
70	Yes	480	do	Very Good.
80	Yes	480	do	Excellent.

* Less than 1 second.

It will be noted from Table II that all the polyethylene wax-zinc oxide coatings containing 65% of pigment or more can be written on with ordinary ball point pen. All the coatings maintain their initial voltage substantially unchanged for at least 2 minutes. All discharge immediately upon reversal of charge, all the coatings comprising 60% or more of photosenstive zinc oxide pigment in the coating give acceptable reproduction of the electrostatic image, those of higher proportions of pigment yielding superior images.

Example 7

A coating composition was prepared by melting in a colloid mill, 35 parts of a polyethylene wax having an average molecular weight of 2,000, melting point about 219–226° F. and viscosity at 140° C. of 180 centipoises. The temperature of the melted wax was raised to 300–350° F. and maintained in this temperature range during gradual addition with agitation, of 65 parts of photosensitive zinc oxide of particle size 0.40μ. After completion of addition of zinc oxide, agitation and temperature were maintained for about an hour to thoroughly blend the components. After blending, the coating composition was allowed to stand quiescent at 300° F. until gas bubbles, which had become entrapped during mixing, were substantially dissipated. The resulting composition was tested for apparent viscosity in a Brookfield viscometer at various temperatures and spindle speeds with results shown in Table III below.

TABLE III

Spindle Speed, r.p.m.	Temp., ° F.	Apparent Viscosity, centipoises
12	300	12,200
	320	11,800
	350	11,200
30	300	8,200
	320	7,700
	350	7,000
60	300	6,100
	320	5,800
	350	5,200

The compositions of the invention thus have excellent electrical properties and they maintain the zinc oxide in excellent suspension. They have fair adhesion to the paper substrate which can be improved by the addition of small quantities of compatible tacky modifiers such as polybutene and tacky resins of the terpene type. Usually proportions of 5–10% or less of such tackifiers are sufficient. If desired, small proportions of toners or other additives may be used, but these should be of such character as not to detract from the desirable electrical properties of the coating or unduly increase its melt viscosity. In general, not more than about 10% of the vehicle of the coating composition will be made up of such additives, i.e. at least about 90% of the total binder will consist of polyethylene wax.

While the above describes the preferred embodiments of my invention, it will be understood that departures may be made therefrom within the scope of the specification and claims.

I claim:

1. A photoconductive insulating coating composition suitable for electrostatic printing purposes comprising at least about 60% by weight of a finely divided photoconductor dispersed in a normally solid polyethylene wax vehicle, said polyethylene wax being a mixture of individual homologs having the structural formula

$$CH_3(C_2H_4)_nC(OH)(CH_3)_2$$

wherein n is an integer having an average value appropriate to provide an average molecular weight between about 1,000 and about 3,000, said composition being solid at temperatures up to about 100° C. and having melt viscosity and thixotropic properties providing sufficient fluidity for coating by the curtain coating method.

2. The composition according to claim 1 wherein said vehicle comprises at least about 90% polyethylene wax having a viscosity at 140° C. between about 50 and about 1,000 centipoises.

3. A base sheet coated with at least about 20 pounds per ream of the composition defined in claim 1.

4. A base sheet coated with at least about 20 pounds per ream of the composition defined in claim 2.

5. A photoconductive insulating coating composition comprising at least about 60% by weight of a photoconductive zinc oxide dispersed in a normally solid vehicle comprising polyethylene wax, said polyethylene wax being a mixture of individual homologs having the structural formula

$$CH_3(C_2H_4)_nC(OH)(CH_3)_2$$

wherein n is an integer having an average value appropriate to provide an average molecular weight between about 1,000 and about 3,000 and viscosity at 140° C. of not more than about 1,000 centipoises, said polyethylene wax constituting at least about 90% of the vehicle portion of said coating composition, said coating composition having a viscosity at 350° F. sufficiently low for application by hot melt coating techniques.

6. The composition according to claim 1 wherein the photoconductive zinc oxide has an average particle size between about 0.39 micron and about 0.41 micron.

7. A base coated with at least about 20 pounds per ream of a photoconductive insulating composition comprising at least about 60% by weight of a photoconductive zinc oxide dispersed in a [illegible]ally solid vehicle comprising polyethylene wax, said polyethylene wax being a mixture of individual homologs having the structural formula

$$CH_3(C_2H_4)_nC(OH)(CH_3)_2$$

wherein n is an integer having an average value appropriate to provide an average molecular weight between about 1,000 and about 3,000 and viscosity at 140° C. between about 50 centipoises and about 1,000 centipoises, said polyethylene wax constituting at least about 90% of the vehicle portion of said coating composition.

8. A process for electrostatic printing which comprises producing a latent electrostatic image on the surface of a photoconductive insulating material comprising a layer constituting at least about 20 pounds per ream of substrate of a composition comprising at least about 60% of a finely divided photoconductive zinc oxide dispersed in a vehicle comprising polyethylene wax, said polyethylene wax being a mixture of individual homologs having the structural formula

$$CH_3(C_2H_4)_nC(OH)(CH_3)_2$$

wherein n is an integer having an average value appropriate to provide an average molecular weight between about 1,000 and about 3,000, said polyethylene wax constituting at least about 90% of said vehicle, and thereafter developing said latent image.

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